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Preparation of 110K (Bi, Pb)-Sr-Ca-Cu-O Superconductor From Glass Precursor

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PREPARATION OF 110K (Bi,Pb)-Sr-Ca-Cu-O SUPERCONDUCTOR FROM GLASS PRECURSOR

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SUMMARY

The $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ glass, prepared by rapid quenching of the melt, showed T_g of 383°C , crystallization temperature of $\sim 446^\circ\text{C}$, melting temperature of $\sim 855^\circ\text{C}$, and bulk density of 5.69g/cm^3 in air. The as-quenched glass was oxygen-deficient. On heating in O_2 , it showed a slow, irreversible, and continuous weight gain starting at $\sim 530^\circ\text{C}$. The influence of annealing conditions on the formation of various phases has been investigated by XRD and electrical resistivity measurements. The 110K- T_c phase did not form below 840°C . The amount of this phase increased with the sintering time at 840°C . A sample annealed at 840°C for 243h in air and furnace cooled showed the highest $T_c(R=0)$ of 107.2K and transition width $\Delta T_c(10-90\%)$ of $\sim 2\text{K}$.

INTRODUCTION

Since the discovery of oxide high temperature superconductors (HTS), various novel processing methods are

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being explored for their fabrication in diverse shapes and geometries. Long continuous HTS wires having good mechanical strength, high critical temperatures (T_C), and high critical current densities are needed for various practical applications such as superconducting magnets, electric motors, electric power transmission lines, electric power storage, etc.

Drawing glass fibers from melts is a well established technique in the glass industry which may also be employed for fabrication of the HTS fibers. Before this could actually be done, however, it is desirable to understand glass formation in the superconducting oxide systems and crystallization of the superconducting phase(s) in the resulting glasses on thermal treatment. The glass ceramic approach for fabrication of the HTS in the Bi-system has been studied by a number of researchers¹⁻⁶.

The objective of the present study was to melt glass of $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ composition and optimize the subsequent annealing conditions for converting the glass into a high temperature superconductor having a large fraction of the 110K- T_C phase.

EXPERIMENTAL

The experimental procedure was essentially the same as described earlier^{2,3}. Briefly speaking, calculated amounts

of Bi_2O_3 , PbO_2 , SrCO_3 , CaO , and CuO were slurry mixed in acetone, calcined in air at $\sim 800^\circ\text{C}$ overnight, cooled and reground. The mixture was melted in a covered Pt crucible at $\sim 1025^\circ\text{C}$ for $\sim 0.5\text{h}$. The melt was fast quenched by pressing between two copper plates resulting in dark sheets $\sim 1\text{mm}$ thick which were found to be amorphous (Fig. 1) from powder x-ray diffraction (XRD) along with the presence of low intensity peaks of CaO . From atomic absorption, chemical composition of the glass was found to be within 1% of the nominal composition.

Thermogravimetric analysis (TGA) was carried out under oxygen or nitrogen flow at heating and cooling rates of $5^\circ\text{C}/\text{min}$ using a Perkin-Elmer TGS-2 system. A Perkin-Elmer DTA 1500 system was used for differential thermal analysis (DTA) at a heating rate of $10^\circ\text{C}/\text{min}$ in air. Glass density was measured from the immersion method using water. Crystalline phases formed in the annealed glass specimens were identified from powder XRD. Microstructures of polished samples were observed in a JEOL JSM-840A scanning electron microscope (SEM). X-ray dot mapping of various elements and the EDAX analysis were carried out using a Kevex Delta Class Analyzer. Electrical resistance as a function of temperature was measured to 60K by the standard four probe technique using a current density of $\sim 0.1\text{A}/\text{cm}^2$. Silver paint was used to attach the leads.

RESULTS AND DISCUSSION

TGA curves of the glass in N_2 and O_2 atmospheres at the heating and cooling rates of $5^\circ\text{C}/\text{min}$ are given in Fig. 2. In nitrogen the sample starts losing weight at $\sim 750^\circ\text{C}$, the total weight loss being 0.53% when heated to 850°C . When the sample is held at this temperature a further loss in weight is observed. This weight loss at high temperature where the sample starts melting may be due to loss of oxygen. These Bi compounds are known to melt at lower temperatures in inert atmosphere than in oxygen. On cooling to ambient temperature, almost no further change in weight is noticed. In contrast, in O_2 there is a slow and continuous weight gain starting at $\sim 530^\circ\text{C}$ which reaches a plateau at $\sim 820^\circ\text{C}$. The total gain in weight was 2.1%. There was no further weight change on cooling. These results indicate that the as-quenched glass is oxygen-deficient.

From DTA, the glass transition temperature, T_g , the crystallization peak temperature, T_p , and the melting temperature, T_m , of the glass were found to be, 383, 446, and 855°C , respectively. Bulk density of the as-quenched glass was measured to be $5.69\text{g}/\text{cm}^3$.

Glass specimens were heat treated in air at various temperatures for different lengths of time as shown in Table

I. Various phases present in the crystallized samples were identified from powder XRD. Typical XRD patterns for three samples annealed for various times at 840°C in air are presented in Fig. 3 and the results are summarized in Table I. All samples are seen to be multiphase. On heating the glass, $\text{Bi}_2\text{Sr}_2\text{Ca}_0\text{Cu}_1\text{O}_6$ (2201) crystallizes out first followed by formation of the 80K $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ (2212) phase at higher temperature. The 110-K T_C phase, probably $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223), starts appearing in samples annealed at temperatures close to the melting point, probably by reaction between the phases formed at lower temperatures. Fraction of the 2223 phase increased with the time of annealing at 840°C. This indicates sluggish kinetics of the high- T_C phase formation probably due to the relatively long range diffusive ordering involved. The TGA curve in O_2 (Fig. 2) shows that formation of the 2212 phase is accompanied by absorption of O_2 and no further uptake of O_2 occurs when the high- T_C 2223 phase is produced at $\sim 840^\circ\text{C}$.

Temperature dependence of the electrical resistance of each annealed glass sample was measured to 63K. Values of T_C for various samples are listed in Table I. The plot for sample BI-9 which was annealed at 840°C for 243h and furnace cooled in air is shown in Fig. 4. This shows a metallic behavior at higher temperatures, with a sharp drop in resistance starting at $\sim 115\text{K}$, with $T_C(R = 0)$ of 107.2K, and

transition width ΔT_c (10-90%) of $\sim 2K$. An increase in annealing temperature to $850^\circ C$ (sample BI-8) had an adverse affect on T_c due to partial melting. The advantages of slow cooling over fast quenching after thermal annealing is evident from comparison of the T_c results for samples BI-6 and BI-7.

Figure 5 shows the scanning electron micrograph and x-ray dot maps of each element taken on the polished surface of sample BI-6 which was annealed for 94h at $840^\circ C$ in air and furnace cooled. The light and dark grey regions in the micrograph are deficient in Bi and Pb. These regions may be further classified as Cu-rich and Ca-rich. The Ca-rich areas are also deficient in Sr. A small region is highly rich in Sr which from EDAX analysis was found to consist almost entirely of Sr (SrO). Similar nonhomogeneous regions were also observed even in the specimen annealed for 243h at $840^\circ C$.

It appears to be difficult to prepare homogeneous single phase 2223 material by the present approach. The advantage of the starting components being intimately mixed in the melt is lost as the 2223 phase does not precipitate out directly from the glass but is preceded by the crystallization of other phases.

SUMMARY AND CONCLUSIONS

The oxygen deficient $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ glass exhibited a slow and irreversible weight gain on heating in oxygen. The kinetics of 110K- T_C phase formation in the glass at 840°C was very sluggish. A specimen annealed at this temperature for more than 10 days in air showed the highest $T_C(R = 0)$ of 107.2K and transition width $\Delta T_C(10-90\%)$ of ~2K. The high- T_C phase did not precipitate out directly from the glass matrix but is produced by reaction between the phases formed at lower temperatures. The glass precursor approach does not seem to be advantageous over the ceramic powder processing method for formation of homogeneous single phase 2223 material.

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REFERENCES

1. T.Komatsu, R.Sato, C.Hirose, K.Matusita, and T.Yamashita, "Preparation of High- T_c Superconducting Bi-Pb-Sr-Ca-Cu-O Ceramics by the Melt Quenching Method," Jpn. J. Appl. Phys., 27[12] L2293-95 (1988).
2. N.P.Bansal and D.E.Farrell, "Glass-Derived Superconducting Ceramics With Zero Resistance at 107K in the $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ System," Appl. Phys. Lett., 55[15] 1572-1574 (1989).
3. N.P.Bansal and M.R.De Guire, "Superconducting Ceramics in the $\text{Bi}_{1.5}\text{SrCaCu}_2\text{O}_x$ System by Melt Quenching Technique," NASA CR-185139 (1989).
4. D.Shi, M.Blank, M.Patel, D.G.Hinks, A.W.Mitchell, K.Vandervoort, and H.Claus, "110K Superconductivity in Crystallized Bi-Sr-Ca-Cu-O Glasses," Physica C, 156[5] 822-26 (1988).
5. H.Zheng and J.D.Mackenzie, " $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_{16}$ Glass and Superconducting Glass Ceramics," Phys. Rev., B38[10] 7166-68 (1988).
6. K.Nassau, A.E.Miller, and E.M.Gyorgy, "Crystallization of a Rapidly Quenched High T_c Bi-Containing Glass Composition," Mat. Res. Bull., 24[6] 711-16 (1989).

Table I. Transition Temperatures and the Phases Formed in
 $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ Glass Samples Annealed in Air
Under Different Conditions

Sample	Heat Temp. (°C)	Treatment Time (h)	Cooling Rate	$T_c(R=0)$ (K)	Phases Identified From Powder XRD
BI-0	-	-	-	-	Amorphous, CaO(trace)
BI-1	500	24	Slow	-	2201 ^a
BI-2	720	24	Slow	75	2212 ^b , 2201, Ca_2PbO_4 , CuO
BI-3	750	24	Slow	<63	2212, 2201, Ca_2PbO_4 , CuO
BI-4	802	25	Slow	69	2212, 2201, Ca_2PbO_4 , CuO
BI-5	840	24	Slow	68	2212, 2223 ^c , 2201, Ca_2PbO_4
BI-6	840	94	Slow	98	2223, 2212, 2201, Ca_2PbO_4
BI-7	840	94	Fast	68	2223, 2212, Ca_2PbO_4
BI-9	840	243	Slow	107.2	2223, 2212, Ca_2PbO_4
BI-8	850	94	Slow	<77	2212, 2223, Ca_2PbO_4

^a $\text{Bi}_2\text{Sr}_2\text{Ca}_0\text{Cu}_1\text{O}_6$

^b $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$

^cHigh- T_c phase isomorphous with $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

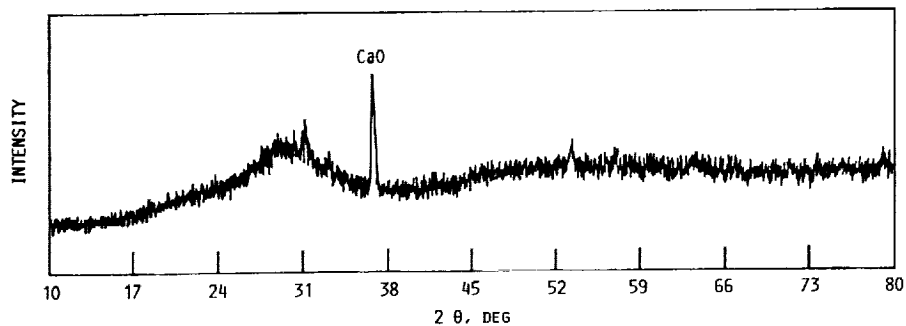


FIGURE 1. - POWDER X-RAY DIFFRACTION OF THE AS-QUENCHED GLASS OF $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ COMPOSITION.

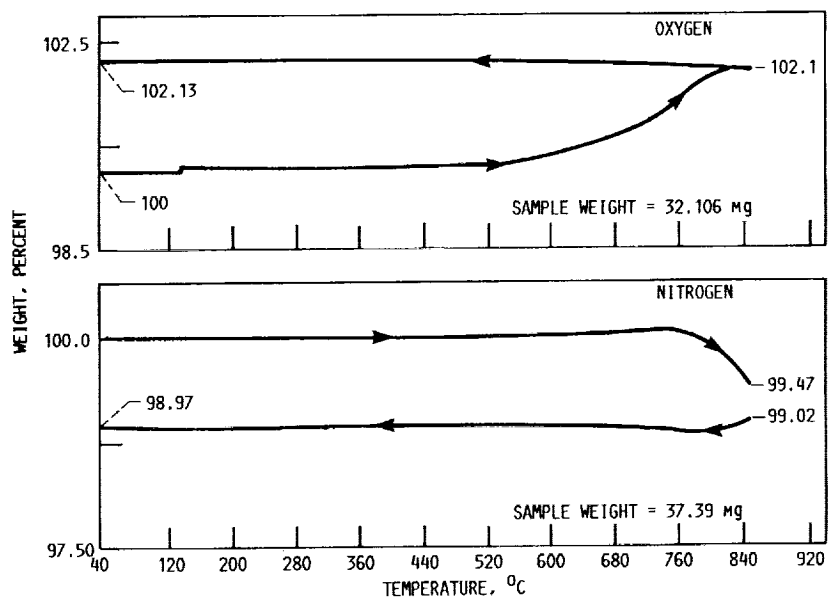


FIGURE 2. - TGA CURVES FOR THE $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ GLASS AT THE HEATING AND COOLING RATES OF $5^\circ\text{C}/\text{MIN}$ IN O_2 AND N_2 .

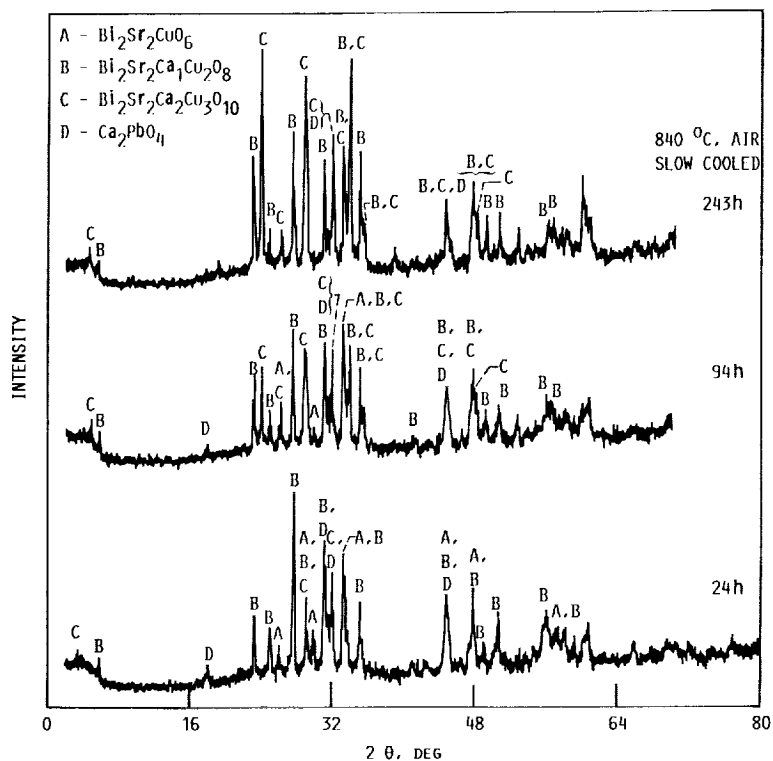


FIGURE 3. - POWDER X-RAY DIFFRACTION SPECTRA OF $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ GLASS SPECIMENS ANNEALED FOR VARIOUS TIMES AT 840°C IN AIR AND FURNACE COOLED.

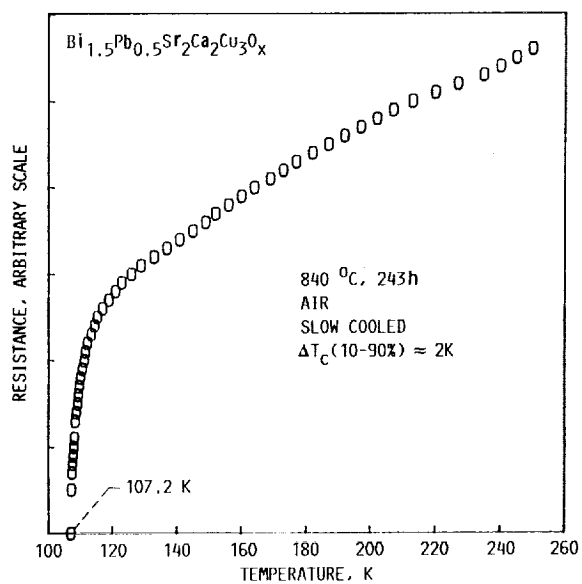


FIGURE 4. - TEMPERATURE DEPENDENCE OF ELECTRICAL RESISTANCE OF $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ GLASS SAMPLE ANNEALED AT 840°C FOR 243h IN AIR AND SLOW COOLED.

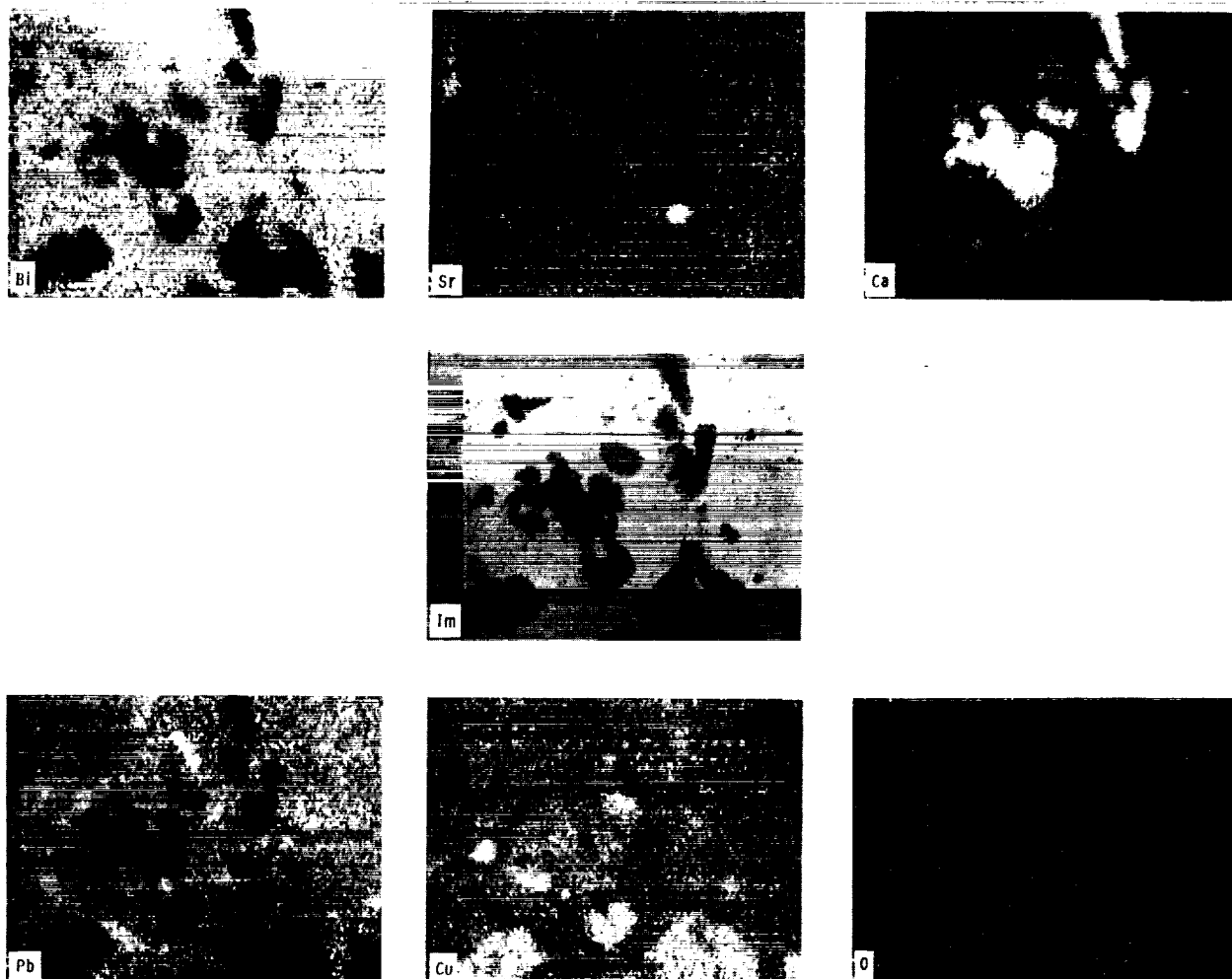


FIGURE 5. - SEM MICROGRAPH AND X-RAY DOT MAPS OF VARIOUS ELEMENTS TAKEN ON THE POLISHED SURFACE OF THE $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ GLASS ANNEALED AT 840°C FOR 94h IN AIR AND FURNACE COOLED.

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